

DESCRIPTION

PHOTORESIST RESIN AND PHOTORESIST RESIN COMPOSITION

5 Technical Field

The present invention relates to a photoresist resin that is useful for the preparation of photoresist resin compositions typically used in fine patterning of semiconductors, and to a photoresist resin composition prepared from the photoresist resin and to a method for the preparation thereof.

Background Art

Positive photoresists for use in manufacturing processes of semiconductors must concurrently have different characteristics such as a characteristic that an exposed portion is made soluble in alkali by the application of light, adhesion to silicon wafers, plasma-etching resistance, and transparency to light used. The positive photoresists are generally used as a solution containing a base polymer, a light-activatable acid generator, and several types of additives for controlling the above characteristics. The wavelength of a light source for light irradiation in lithography for use in semiconductor manufacturing becomes shorter and shorter in recent years, and ArF excimer laser with a wavelength of 193 nm is promising as a next-generation light source. Various polymers containing

a constitutional repeating unit having a group capable of partially leaving by the action of an acid to thereby become soluble in an alkali, and a constitutional repeating unit containing an alicyclic skeleton having a polar group have been
5 proposed as resist polymers for use in the ArF excimer laser exposure system, for example in Japanese Unexamined Patent Application Publications No. 2000-26446 and No. 09-73137.

These polymers are generally prepared by polymerizing a mixture of monomers and separating the target polymers by
10 precipitating the polymerization reaction mixture. When these polymers are to be dissolved in solvents for resist, however, part of them remains insoluble to cause turbidity, although major part of them are dissolved. The insoluble matter may cause troubles or problems in manufacturing processes of
15 semiconductors and must be removed by filtration. However, the insoluble matter comprises fine particles and it takes much time and efforts to remove them by filtration.

Disclosure of Invention

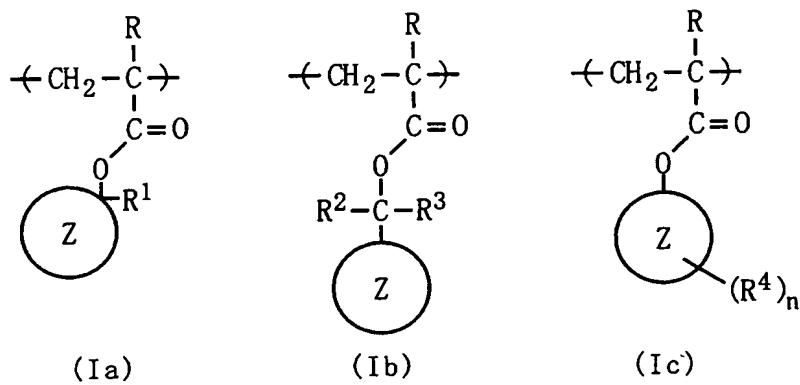
20 Accordingly, an object of the present invention is to provide a photoresist resin that is highly soluble in a solvent for resist. Another object of the present invention is to provide a photoresist resin composition containing the photoresist resin dissolved in a solvent, and a preparation
25 process thereof.

After intensive investigations to achieve the above objects, the present inventors have found (i) that, when a photoresist resin for an ArF excimer laser system is synthetically prepared by dropping polymerization, the 5 resulting polymer exhibits a relatively narrow distribution in molecular weight and has a weight-average molecular weight within a range of 3000 to 15000, but even this polymer causes turbidity (insoluble matter) when dissolved in a solvent for resist; (ii) that the content of polymers (polymer fractions) 10 each having a molecular weight exceeding a specific level (4×10^4) can be significantly reduced by adding a solution of monomers and a solution of a polymerization initiator dropwise from different vessels in dropping polymerization; and (iii) that a resin thus prepared has a content of polymer fractions each 15 having a molecular weight exceeding a specific level (4×10^4) at a specific level (4 percent by weight) or less is easily dissolved in a solvent for resist and is free from turbidity. The present invention has been accomplished based on these findings.

20 Specifically, the present invention provides a photoresist resin comprising at least a constitutional repeating unit A containing a group capable of partially leaving by the action of an acid to thereby become soluble in an alkali; and a constitutional repeating unit B containing an alicyclic 25 skeleton having a polar group, wherein the resin has a

weight-average molecular weight of 3000 to 15000 and has a content of polymer fractions each having a molecular weight exceeding 40000 of 4 percent by weight or less of the total resin.

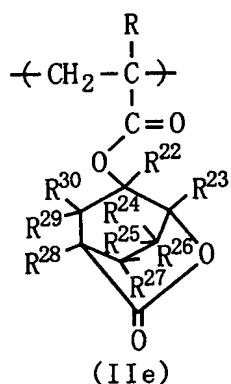
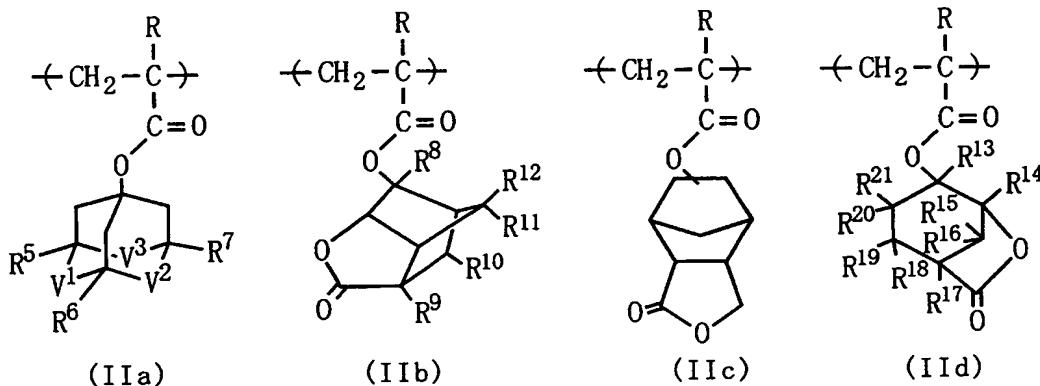
5 The constitutional repeating unit A may be, for example, at least one selected from constitutional repeating units of following Formulae (Ia), (Ib) and (Ic):



wherein Ring Z is an alicyclic hydrocarbon ring having six to
10 twenty carbon atoms which may be substituted; R is hydrogen
atom or an alkyl group having one to six carbon atoms; R¹, R²
and R³ may be the same as or different from one another and are each an alkyl group having one to six carbon atoms; R⁴'s
are substituents combined with Ring Z, may be the same as or
15 different from each other and are each oxo group, an alkyl group,
a hydroxyl group which may be protected by a protective group,
a hydroxyalkyl group which may be protected by a protective
group, or a carboxyl group which may be protected by a protective
group, wherein at least one of nR⁴'s is a -COOR^a group, wherein

R^a is a tertiary hydrocarbon group which may be substituted, tetrahydrofuryl group, tetrahydropyranyl group or oxepanyl group; and n is an integer of 1 to 3.

The constitutional repeating unit B may be, for example,
5 at least one selected from constitutional repeating units of
following Formulae (IIa), (IIb), (IIc), (IId) and (IIe):



wherein R is hydrogen atom or an alkyl group having one to six carbon atoms; R⁵, R⁶ and R⁷ may be the same as or different from
10 one another and are each hydrogen atom, an alkyl group, a hydroxyl group which may be protected by a protective group, a hydroxyalkyl group which may be protected by a protective group,

or a carboxyl group which may be protected by a protective group; V¹, V² and V³ may be the same as or different from one another and are each -CH₂-, -CO- or -COO-, wherein (i) at least one of V¹, V² and V³ is -CO- or -COO-, or (ii) at least one of R⁵,
5 R⁶ and R⁷ is a hydroxyl group which may be protected by a protective group, a hydroxyalkyl group which may be protected by a protective group, or a carboxyl group which may be protected by a protective group; R⁸, R⁹, R¹⁰, R¹¹ and R¹² may be the same as or different from one another and are each hydrogen atom,
10 an alkyl group, a hydroxyl group which may be protected by a protective group, a hydroxyalkyl group which may be protected by a protective group, or a carboxyl group which may be protected by a protective group; R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰ and
R²¹ may be the same as or different from one another and are
15 each hydrogen atom, an alkyl group, a hydroxyl group which may be protected by a protective group, a hydroxyalkyl group which may be protected by a protective group, or a carboxyl group which may be protected by a protective group; and R²², R²³, R²⁴,
R²⁵, R²⁶, R²⁷, R²⁸, R²⁹ and R³⁰ may be the same as or different
20 from one another and are each hydrogen atom, an alkyl group, a hydroxyl group which may be protected by a protective group, a hydroxyalkyl group which may be protected by a protective group, or a carboxyl group which may be protected by a protective group.

25 The present invention further provides a photoresist resin

composition, as a solution comprising the photoresist resin and a light-activatable acid generator in a solvent.

In addition, the present invention provides a process for preparing a photoresist resin composition, comprising the step
5 of dissolving the photoresist resin in a solvent.

In the present description, the terms "acrylic" and "methacrylic" may be generically referred to as "(meth)acrylic", and the terms "acryloyl" and "methacryloyl" may be generically referred to as "(meth)acryloyl". Protective groups
10 conventionally used in the field of organic synthesis can be used as the protective groups for, for example, hydroxyl group and carboxyl group.

The photoresist resin of the present invention is very highly soluble in solvents for resist and contributes to
15 efficient preparation of a photoresist resin composition, in which the step of filtrating solvent-insoluble matter can be omitted or simplified.

Best Mode for Carrying Out the Invention

20 The photoresist resin of the present invention comprises at least a constitutional repeating unit A containing a group capable of partially leaving by the action of an acid to thereby become soluble in an alkali, and a constitutional repeating unit B containing an alicyclic skeleton having a polar group.
25 The constitutional repeating unit A containing a group

capable of partially leaving by the action of an acid to thereby become soluble in an alkali is not specifically limited, as long as it is a constitutional repeating unit, part of which will leave by the action of an acid generated from a
5 light-activatable acid generator upon irradiation with light or radiation (a constitutional repeating unit having an acid-induced leaving group). Examples of the constitutional repeating unit A are constitutional repeating units corresponding to (meth)acrylic esters each containing an
10 alicyclic hydrocarbon group having six to twenty carbon atoms and having a group capable of leaving by the action of an acid (constitutional repeating units formed by polymerization at carbon-carbon double bonds). The "(meth)acrylic esters each containing an alicyclic hydrocarbon group having six to twenty
15 carbon atoms and having a group capable of leaving by the action of an acid" include a (meth)acrylate ester containing an alicyclic hydrocarbon group having six to twenty carbon atoms and having a tertiary carbon atom at the bonding site with an oxygen atom constituting the ester bond of the (meth)acrylic ester. The
20 alicyclic hydrocarbon group may be bonded to the oxygen atom constituting the ester bond of the (meth)acrylic ester directly or with the interposition of a linkage group such as an alkylene group. The alicyclic hydrocarbon group having six to twenty carbon atoms may be a monocyclic hydrocarbon group or a
25 polycyclic (bridged) hydrocarbon group. Typical examples of

the units corresponding to the (meth)acrylic esters are units represented by Formulae (Ia) and (Ib).

The "(meth)acrylic esters each containing an alicyclic hydrocarbon group having six to twenty carbon atoms and having 5 a group capable of leaving by the action of an acid" also include (meth)acrylic esters each having an alicyclic hydrocarbon group having six to twenty carbon atoms, wherein a -COOR^a group is bonded to the alicyclic hydrocarbon group directly or with the interposition of a linkage group, wherein R^a is a tertiary 10 hydrocarbon group which may be substituted, tetrahydrofuryl group, tetrahydropyranyl group or oxepanyl group. Examples of the tertiary hydrocarbon group in R^a of the -COOR^a group are t-butyl, t-amyl, 2-methyl-2-adamantyl, and (1-methyl-1-adamantyl)ethyl groups. Examples of 15 substituents which the tertiary hydrocarbon group may have are halogen atoms, alkyl groups such as alkyl groups having one to four carbon atoms, a hydroxyl group which may be protected by a protective group, oxo group, and a carboxyl group which may be protected by a protective group. In R^a, the 20 tetrahydrofuryl group, the tetrahydropyranyl group and the oxepanyl group include 2-tetrahydrofuryl group, 2-tetrahydropyranyl group and 2-oxepanyl group, respectively. Examples of the linkage group are alkylene groups such as linear or branched alkyl groups each having one to six carbon atoms. 25 The alicyclic hydrocarbon group may be bonded to the oxygen

atom constituting the ester bond of the (meth)acrylic ester directly or with the interposition of a linkage group such as an alkylene group. The alicyclic hydrocarbon group having six to twenty carbon atoms may be a monocyclic hydrocarbon group 5 or a polycyclic (bridged) hydrocarbon group. Typical examples of the units corresponding to these (meth)acrylic esters are units represented by Formula (Ic).

Constitutional repeating units corresponding to (meth)acrylic esters each containing a lactone ring having an 10 oxygen atom constituting an ester bond at the beta-position of the lactone ring, and at least one hydrogen atom at the alpha-position of the lactone ring (constitutional repeating units undergone polymerization at a carbon-carbon double bond), for example, can also be used as the constitutional repeating 15 unit A containing a group capable of partially leaving by the action of an acid to thereby become soluble in an alkali. Each of these constitutional repeating units A can be used alone or in combination.

The constitutional repeating unit A is preferably at least 20 one selected from constitutional repeating units of Formulae (Ia), (Ib) and (Ic). In Formulae (Ia), (Ib) and (Ic), the alicyclic hydrocarbon ring having six to twenty carbon atoms in Ring Z may be any of monocyclic rings and polycyclic rings such as fused rings and bridged rings. Typical examples of 25 the alicyclic hydrocarbon ring are cyclohexane ring,

cyclooctane ring, cyclodecane ring, adamantane ring,
norbornane ring, norbornene ring, bornane ring, isobornane ring,
perhydroindene ring, decalin ring, perhydrofluorene ring
(tricyclo[7.4.0.0^{3,8}]tridecane ring), perhydroanthracene ring,
5 tricyclo[5.2.1.0^{2,6}]decane ring, tricyclo[4.2.2.1^{2,5}]undecane
ring and tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodecane ring. The
alicyclic hydrocarbon ring may have one or more substituents.
Examples of such substituents are alkyl groups including alkyl
groups each having one to four carbon atoms such as methyl group;
10 halogen atoms such as chlorine atom; a hydroxyl group which
may be protected by a protective group; oxo group; and a carboxyl
group which may be protected by a protective group. Ring Z
is preferably, for example, a polycyclic alicyclic hydrocarbon
ring (bridged hydrocarbon ring) such as adamantane ring.

15 Examples of the alkyl groups each having one to six carbon
atoms as R in Formulae (Ia), (Ib) and (Ic), and as R¹, R² and
R³ in Formulae (Ia) and (Ib) are linear or branched alkyl groups
each having one to six carbon atoms, such as methyl, ethyl,
propyl, isopropyl, butyl, isobutyl, s-butyl, t-butyl and hexyl
20 groups. R is preferably hydrogen atom or an alkyl group having
one to three carbon atoms, of which hydrogen atom or methyl
group is typically preferred. Examples of the alkyl group as
R⁴ in Formula (Ic) are linear or branched alkyl groups each
having about one to about twenty carbon atoms, such as methyl,
25 ethyl, propyl, isopropyl, butyl, isobutyl, s-butyl, t-butyl,

hexyl, octyl, decyl and dodecyl groups. Examples of the hydroxyl group which may be protected by a protective group as R⁴ are hydroxyl group and substituted oxy groups including alkoxy groups each having one to four carbon atoms, such as 5 methoxy, ethoxy and propoxy groups. Examples of the hydroxyalkyl group which may be protected by a protective group are groups each comprising the hydroxyl group which may be protected by a protective group combined with the interposition of an alkylene group having one to six carbon atoms. Examples 10 of the carboxyl group which may be protected by a protective group are -COOR^b groups, wherein R^b is hydrogen atom or an alkyl group. Examples of the alkyl group herein are linear or branched alkyl groups each having one to six carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, s-butyl, t-butyl 15 and hexyl groups. R^a of the -COOR^a group in R⁴ is as defined above.

The constitutional repeating unit B containing an alicyclic skeleton having a polar group includes (1) monomer units B1 (constitutional repeating units formed by 20 polymerization at carbon-carbon double bonds) corresponding to (meth)acrylic esters each having an alicyclic hydrocarbon group bonded to an oxygen atom constituting the ester bond, which alicyclic hydrocarbon group contains a lactone ring and has six to twenty carbon atoms. The alicyclic hydrocarbon group 25 herein includes, for example, a group comprising a lactone ring

fused with a monocyclic or polycyclic (bridged) alicyclic carbon ring. Typical examples of such constitutional repeating units B1 are units of Formula (IIa) wherein at least one of V¹, V² and V³ is -COO-, and units represented by Formulae (IIb), (IIc), 5 (IId) and (IIe).

The constitutional repeating unit B containing an alicyclic skeleton having a polar group also includes (2) monomer units B2 (constitutional repeating units formed by polymerization at carbon-carbon double bonds) corresponding 10 to (meth)acrylic esters each having an alicyclic hydrocarbon group bonded to an oxygen atom constituting the ester bond. The alicyclic hydrocarbon group herein contains a polar group such as hydroxyl group, carboxyl group or oxo group and has six to twenty carbon atoms. Among such alicyclic hydrocarbon 15 groups, a bridged hydrocarbon group is preferred herein. Typical examples of such constitutional repeating units B1 are units of Formula (IIa) wherein at least one of V¹, V² and V³ is -CO-, or at least one of R⁵, R⁶ and R⁷ is a hydroxyl group which may be protected by a protective group, a hydroxyalkyl 20 group which may be protected by a protective group, or a carboxyl group which may be protected by a protective group.

The constitutional repeating unit B imparts, to the resin, adherence typically with silicon wafers by the action of the polar group and dry etching resistance by the action of the 25 alicyclic skeleton. Each of the constitutional repeating units

B may be contained alone or in combination. The constitutional repeating unit B is preferably at least one selected from the constitutional repeating units Formulae (IIa), (IIb), (IIc), (IId) and (IIe). The combination use of the constitutional repeating unit B1 and the constitutional repeating unit B2 can advantageously yield a resin which exhibits well-balanced properties such as substrate adherence, dry etching resistance and solubility in solvents for resist and has excellent and uniform reactivity in polymerization. Namely, the resulting polymer is highly uniform in its molecular weight and molecular structure.

R in Formulae (IIa), (IIb), (IIc), (IId) and (IIe) is has the same meaning as R in Formulae (Ia), (Ib) and (Ic). In Formulae (IIa) through (IIe), examples of the alkyl groups as R⁵ through R³⁰ are linear or branched alkyl groups each having one to thirteen carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, s-butyl, t-butyl, hexyl, octyl, decyl and dodecyl groups. Among them, alkyl groups each having one to four carbon atoms are preferred. Examples of the hydroxyl group which may be protected by a protective group are hydroxyl group and substituted oxy groups including alkoxy groups each having one to four carbon atoms, such as methoxy, ethoxy and propoxy groups. Examples of the hydroxyalkyl group which may be protected by a protective group are groups each comprising the hydroxyl group which may be protected by a protective group

combined with the interposition of an alkylene group having one to six carbon atoms. Examples of the carboxyl group which may be protected by a protective group are $-\text{COOR}^b$ groups, wherein R^b is as defined above.

5 The photoresist resin of the present invention may further comprise any of other constitutional repeating units in addition to the constitutional repeating units A and B, within ranges not adversely affecting the properties such as solubility in an alkali (leaving property by the action of an acid), substrate adherence, dry etching resistance and solubility in solvents for resist. Such other constitutional repeating units are not specifically limited, as long as they are units corresponding to monomers copolymerizable with monomers corresponding to the constitutional repeating unit A and with monomers corresponding to the constitutional repeating unit B and do not adversely affect the properties of the resist. Examples of such units are units corresponding to (meth)acrylic acid or derivatives thereof, maleic acid or derivatives thereof, fumaric acid or derivatives thereof, and cyclic olefins. Examples of the (meth)acrylic acid or derivatives thereof are (meth)acrylic esters each having a lactone ring such as γ -butyrolactone ring or δ -valerolactone ring. Specific examples thereof are α -(meth)acryloyloxy- γ -butyrolactone, α -(meth)acryloyloxy- α -methyl- γ -butyrolactone and
10 20 25 α -(meth)acryloyloxy- γ,γ -dimethyl- γ -butyrolactone. These

(meth)acrylic esters each having a lactone ring can impart, to the polymer, adherence to a substrate.

The content of the constitutional repeating unit A in the photoresist resin of the present invention is, for example, 5 from 5 to 90 percent by mole, preferably from 10 to 80 percent by mole, and more preferably from 20 to 70 percent by mole. A content of the constitutional repeating unit A less than 5 percent by mole may invite insufficient dissolution of the resulting resist film in alkali development and may reduce the 10 resolution to thereby fail to produce fine patterns with good accuracy. A content of the constitutional repeating unit A exceeding 90 percent by mole may reduce adherence to a substrate and dry etching resistance and may often invite peeling off of the resulting pattern as a result of development.

15 The content of the constitutional repeating unit B in the photoresist resin of the present invention is, for example, from 10 to 95 percent by mole, preferably from 20 to 90 percent by mole, and more preferably from 30 to 80 percent by mole. A content of the constitutional repeating unit B less than 10 percent by mole may often reduce adherence to a substrate and dry etching resistance. A content of the constitutional repeating unit B exceeding 95 percent by mole may often invite insufficient dissolution of the resist film in alkali development. The ratio of the constitutional repeating unit 20 B1 to the constitutional repeating unit B2, if used in

combination, is not specifically limited but is generally from about 5/95 to about 95/5, preferably from about 10/90 to 90/10, and more preferably from about 30/70 to about 70/30 in terms of molar ratio.

5 One of the key features of the photoresist resin of the present invention is that the resin has a weight-average molecular weight (Mw) of 3000 to 15000 and has a content of polymer fractions each having a molecular weight exceeding 40000 of 4 percent by weight or less (preferably 3 percent by weight
10 or less, and more preferably 2 percent by weight or less). If the weight-average molecular weight is less than 3000, a desired film strength is not obtained in the formation of a resist film. If the weight-average molecular weight exceeds 15000, the resulting photoresist resin composition has an excessively high
15 viscosity as a solution, which invites decreased workability and fails to produce a uniform, good coating. The weight-average molecular weight is preferably from about 4000 to about 14000, and more preferably from about 5000 to about 13000. If the content of polymer fractions each having a
20 molecular weight exceeding 40000 exceeds 4 percent by weight, the resin invites insoluble matter (turbidity) when dissolved in a solvent for resist. If such an insoluble matter hardly soluble in a resist solvent is contained in the photoresist resin, a uniform resist film of homogenous quality is not
25 obtained, the sensitivity and resolution decrease, and a desired

pattern cannot be significantly prepared with good accuracy. To avoid this, the insoluble matter must be removed by filtration. However, the insoluble matter is generally in the form of fine particles (colloid), and it takes much time and efforts to remove
5 it by filtration. This inhibits efficient production of a photoresist resin composition. The molecular weight distribution (M_w/M_n) of the photoresist resin of the present invention is, for example, from about 1.1 to about 3.5 and preferably from about 1.5 to about 3.0, wherein M_n is a
10 number-average molecular weight, and M_n and M_w are in terms of polystyrene. The weight-average molecular weight, the content of polymer fractions each having a molecular weight exceeding 40000, and the molecular weight distribution can be determined by gel permeation chromatography (GPC).

15 The photoresist resin of the present invention can be prepared, for example, by subjecting a monomer solution and a polymerization initiator solution to polymerization at 60°C to 130°C while adding these solutions dropwise from different vessels to a reactor. The monomer solution contains a monomer
20 mixture at least comprising a monomer "a" having a group capable of partially leaving by the action of an acid to thereby become soluble in an alkali, and a monomer "b" containing an alicyclic skeleton having a polar group. The polymerization initiator solution contains a polymerization initiator

25 It is important to add the monomer solution and the

polymerization initiator solution dropwise separately from different vessels to the reactor. This procedure enables the content of polymer fractions each having a molecular weight exceeding 40000 to be reduced to 4 percent by weight or less
5 of the total polymers. In contrast, if a solution containing both the monomers and the polymerization initiator is added dropwise to the reactor, the polymerization of the monomers gradually proceeds in the dropping vessel before dropping to form polymer fractions each having a high molecular weight.
10 Thus, the resulting polymer after the completion of the polymerization contains more than 4 percent by weight of polymer fractions each having a molecular weight exceeding 40000.

The polymerization temperature (temperature of a reaction mixture) in the dropping polymerization is preferably
15 controlled so as to minimize the variation or deviation of the polymerization temperature. It is preferred, for example, to control the polymerization temperature (temperature of the reaction mixture) within $\pm 5^{\circ}\text{C}$, more preferably within $\pm 3^{\circ}\text{C}$ of a preset temperature during 93 percent or more, more preferably
20 95 percent or more, of the total dropping time (adding time) of the monomer solution and the polymerization initiator solution. If the polymerization is carried out under such conditions that the polymerization temperature deviates from $\pm 5^{\circ}\text{C}$ of the preset temperature (the variation of the
25 polymerization temperature exceeds $\pm 5^{\circ}\text{C}$) during 7 percent or

more of the total dropping time, the content of polymer fractions each having a molecular weight exceeding 40000 may often increase. Particularly, the deviation of the polymerization temperature may often increase in the early stages of the dropping, since
5 the solutions to be dropped are generally at around room temperature, heat of polymerization generates in a small quantity at the beginning of the dropping, and thereby the polymerization temperature (temperature of the reaction mixture) once significantly falls down from the preset
10 temperature of a control system. Based on this, the polymerization temperature should be preferably controlled within the above-specified narrow deviation, for example, by a process of controlling the temperature in the reactor (liquid temperature) at a temperature higher than the preset temperature
15 before the dropping of the monomer solution and the polymerization initiator solution, and then starting dropping of the solutions. The temperature in the reactor may be set, for example, within a range of [(preset temperature)+1°C to (preset temperature)+5°C], and preferably within a range of
20 [(preset temperature)+1°C to (preset temperature)+3°C]. According to this process, the system temperature begins to gradually decrease upon the initiation of the dropping of the monomer solution and the polymerization initiator solution. At the time when the system temperature reaches the vicinity
25 of the target preset temperature, the temperature set in the

control system is gradually reduced to the target preset temperature. Thus, the system temperature can be stabilized within the target preset temperatures within a short time while avoiding the system temperature from significantly falling 5 below the preset temperature. This prevents polymer fractions each having a high molecular weight exceeding 40000 from forming. In contrast, when the temperature in the reactor is controlled at the target preset temperature at the beginning of the dropping of the solutions, the system temperature falls below the preset 10 temperature at the beginning of the dropping. To cover this, the control system significantly leans toward heating, which causes an increased hunting in the temperature. thus, the polymerization is carried out under such conditions that the 15 polymerization temperature deviates from $\pm 5^{\circ}\text{C}$ of the preset temperature (the variation of the polymerization temperature exceeds $\pm 5^{\circ}\text{C}$) during 7 percent or more (e.g., 30 minutes or more) of the total dropping time. This results in an increased content of polymer fractions each having a high molecular weight exceeding 40000, which exceeds 4 percent by weight of the total 20 polymer.

A process for controlling the polymerization temperature within $\pm 5^{\circ}\text{C}$ of the preset temperature during 93 percent or more of the total dropping time is not limited to the above-mentioned process, and any other process can be employed. The temperature 25 in the system can be prevented from varying, for example, by

dropping the monomer solution and the polymerization initiator solution at low speed in the beginning, and gradually increasing the dropping speed.

The dropping polymerization, more specifically, is carried out by separately preparing a monomer solution comprising a monomer mixture dissolved in an organic solvent (a polymerization solvent), and a polymerization initiator solution comprising a polymerization initiator dissolved in an organic solvent (the polymerization solvent), placing the solutions into different vessels, and adding the monomer solution and the polymerization initiator solution dropwise concurrently to an organic solvent (polymerization solvent) controlled at a specific temperature, respectively. The monomer solution and the polymerization initiator solution are preferably added dropwise at the same rate (speed).

Examples of the polymerization solvent are glycol solvents, ester solvents, ketone solvents, ether solvents, amide solvents, sulfoxide solvents, monohydric alcohol solvents, hydrocarbon solvents, and mixtures of these solvents. Examples of the glycol solvents are propylene glycol solvents such as propylene glycol monomethyl ether and propylene glycol monomethyl ether acetate; and ethylene glycol solvents such as ethylene glycol monomethyl ether, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether, ethylene glycol monoethyl ether acetate, ethylene glycol monobutyl ether and ethylene

glycol monobutyl ether acetate. Examples of the ester solvents are lacticester solvents such as ethyl lactate; propionic ester solvents such as methyl 3-methoxypropionate; and acetic ester solvents such as methyl acetate, ethyl acetate, propyl acetate
5 and butyl acetate. Examples of the ketone solvents are acetone, methyl ethyl ketone, methyl isobutyl ketone, methyl amyl ketone and cyclohexanone. Examples of the ether solvents are diethyl ether, diisopropyl ether, dibutyl ether, tetrahydrofuran and dioxane. The amide solvents include, for example,
10 N,N-dimethylformamide. The sulfoxide solvents include, for example, dimethyl sulfoxide. Examples of the monohydric alcohol solvents are methanol, ethanol, propanol and butanol. Examples of the hydrocarbon solvents are toluene, xylenes, hexane and cyclohexane.
15 Preferred polymerization solvents include glycol solvents such as propylene glycol monomethyl ether and propylene glycol monomethyl ether acetate; ester solvents such as ethyl lactate; ketone solvents such as methyl isobutyl ketone and methyl amyl ketone; and mixtures of these solvents. Among them, typically
20 preferred are solvents at least comprising propylene glycol monomethyl ether acetate, such as a solvent containing propylene glycol monomethyl ether acetate alone, a solvent mixture containing propylene glycol monomethyl ether acetate and propylene glycol monomethyl ether, and a solvent mixture
25 containing propylene glycol monomethyl ether acetate and ethyl

lactate.

Any known polymerization initiator can be used as the polymerization initiator herein.

In the dropping polymerization, the ratio of the amount 5 of the solvent to be placed in the reaction system beforehand to the total amount of the solutions (the monomer solution and the polymerization initiator solution) to be added dropwise can be appropriately set in consideration typically of productivity, economical efficiency, workability and 10 operability within ranges not adversely affecting the quality of the resin. In general, the ratio of the solvent to the total amount of the solutions is from 5/95 to 90/10, preferably from 10/90 to 70/30, and more preferably from 20/80 to 60/40 in terms of weight ratio. The total amount of the polymerization 15 solvents to be used, i.e., the total amount of the solvent to be placed in before hand or the amount of the solvent in the solution with the amount of the solvents contained in the solutions to be added dropwise, can be appropriately set in consideration typically of workability, operability, reaction 20 efficiency and solubility of the resulting polymer and is generally from about 100 to about 2000 parts by weight, preferably from about 200 to about 1000 parts by weight, and more preferably from about 300 to about 700 parts by weight, to 100 parts by weight of the total amount of the monomers.

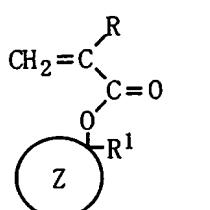
25 The total dropping time for the monomer solution and the

polymerization initiator solution may vary depending on, for example, the polymerization temperature and types of the monomers and is generally from about one to about ten hours, and preferably from about three to about eight hours. The 5 polymerization temperature is difficult to control to thereby often increase the deviation of the polymerization temperature particularly in the first half of the dropping procedure of the monomer solution or the polymerization initiator solution (in the first half of the total dropping time). Accordingly, 10 it is preferred to control the polymerization temperature within $\pm 5^{\circ}\text{C}$, preferably within $\pm 3^{\circ}\text{C}$, of the preset temperature during 95 percent or more in the first half of the dropping time in the dropping procedure of the monomer solution or the polymerization initiator solution. Aging may be carried out 15 at an appropriate temperature (e.g., from 60°C to 130°C) for an appropriate time period (e.g., about 0.1 to about 10 hours, and preferably from bout 1 to about 6 hours) to complete the polymerization.

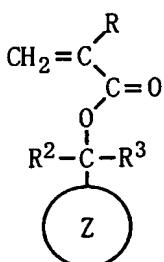
The monomer "a" corresponds to the constitutional 20 repeating unit A, and the monomer "b" corresponds to the constitutional repeating unit B. Such resins containing any of constitutional repeating units represented by Formulae (Ia), (Ib), (Ic), (IIa), (IIb), (IIc), (IID) and (IIe) can be prepared by subjecting corresponding (meth)acrylic esters as comonomers 25 to polymerization.

[Constitutional Repeating Units Represented by Formulae
(Ia), (Ib) and (Ic)]

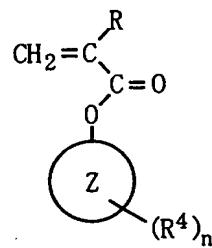
Monomers corresponding to the constitutional repeating units represented by Formulae (Ia), (Ib) and (Ic) are represented 5 by following Formulae (1a), (1b) and (1c), respectively. There can be stereoisomers in the compounds represented by Formulae (1a), (1b) and (1c), and each of these compounds can be used alone or in combination as a mixture.



(1a)



(1b)



(1c)

10 Wherein Ring Z is an alicyclic hydrocarbon ring having six to twenty carbon atoms which may be substituted; R is hydrogen atom or methyl group; R¹, R² and R³ may be the same as or different from one another and are each an alkyl group having one to six carbon atoms; R⁴s are substituents combined with Ring Z, may 15 be the same as or different from each other and are each oxo group, an alkyl group, a hydroxyl group which may be protected by a protective group, a hydroxyalkyl group which may be protected by a protective group, or a carboxyl group which may be protected by a protective group, wherein at least one of 20 nR⁴s is a -COOR^a group, wherein R^a is a tertiary hydrocarbon group which may be substituted, tetrahydrofuryl group,

tetrahydropyranyl group or oxepanyl group; and n is an integer of 1 to 3.

Typical examples of the compounds represented by Formula

(1a) include, but are not limited to, the following compounds.

5 [1-1] 2-(Meth)acryloyloxy-2-methyladamantane (R is H or CH₃; R¹ is CH₃; and Z is adamantane ring)

[1-2] 1-Hydroxy-2-(meth)acryloyloxy-2-methyladamantane (R is H or CH₃; R¹ is CH₃; and Z is adamantane ring having hydroxyl group at the 1-position)

10 [1-3] 5-Hydroxy-2-(meth)acryloyloxy-2-methyladamantane (R is H or CH₃; R¹ is CH₃; and Z is adamantane ring having hydroxyl group at the 5-position)

[1-4] 1,3-Dihydroxy-2-(meth)acryloyloxy-2-methyladamantane (R is H or CH₃; R¹ is CH₃; and Z is adamantane ring having hydroxyl groups at the 1- and 3-positions)

[1-5] 1,5-Dihydroxy-2-(meth)acryloyloxy-2-methyladamantane (R is H or CH₃; R¹ is CH₃; and Z is adamantane ring having hydroxyl groups at the 1- and 5-positions)

20 [1-6] 1,3-Dihydroxy-6-(meth)acryloyloxy-6-methyladamantane (R is H or CH₃; R¹ is CH₃; and Z is adamantane ring having hydroxyl groups at the 1- and 3-positions)

[1-7] 2-(Meth)acryloyloxy-2-ethyladamantane (R is H or CH₃; R¹ is CH₂CH₃; and Z is adamantane ring)

25 [1-8] 1-Hydroxy-2-(meth)acryloyloxy-2-ethyladamantane (R is H or CH₃; R¹ is CH₂CH₃; and Z is adamantane ring having hydroxyl

group at the 1-position)

[1-9] 5-Hydroxy-2-(meth)acryloyloxy-2-ethyladamantane (R is H or CH₃; R¹ is CH₂CH₃; and Z is adamantane ring having hydroxyl group at the 5-position)

5 [1-10] 1,3-Dihydroxy-2-(meth)acryloyloxy-2-ethyladamantane (R is H or CH₃; R¹ is CH₂CH₃; and Z is adamantane ring having hydroxyl groups at the 1- and 3-positions)

[1-11] 1,5-Dihydroxy-2-(meth)acryloyloxy-2-ethyladamantane (R is H or CH₃; R¹ is CH₂CH₃; and Z is adamantane ring having hydroxyl groups at the 1- and 5-positions)

10 [1-12] 1,3-Dihydroxy-6-(meth)acryloyloxy-6-ethyladamantane (R is H or CH₃; R¹ is CH₂CH₃; and Z is adamantane ring having hydroxyl groups at the 1- and 3-positions)

Each of the compounds represented by Formula (1a) can be
15 prepared, for example, by reacting a corresponding cyclic alcohol with (meth)acrylic acid or a reactive derivative thereof according to a conventional esterification procedure using an acid catalyst or a transesterification catalyst.

Typical examples of the compounds represented by Formula
20 (1b) include, but are not limited to, the following compounds.

[1-13] 1-(1-(Meth)acryloyloxy-1-methylethyl)adamantane (R is H or CH₃; R² and R³ are CH₃; and Z is adamantane ring)

[1-14]

1-Hydroxy-3-(1-(meth)acryloyloxy-1-methylethyl)adamantane
25 (R is H or CH₃; R² and R³ are CH₃; and Z is adamantane ring having

hydroxyl group at the 1-position)

[1-15] 1-(1-Ethyl-1-(meth)acryloyloxypropyl)adamantane (R is H or CH₃; R² and R³ are CH₂CH₃; and Z is adamantane ring)

[1-16]

5 1-Hydroxy-3-(1-ethyl-1-(meth)acryloyloxypropyl)adamantane (R is H or CH₃; R² and R³ are CH₂CH₃; and Z is adamantane ring having hydroxyl group at the 1-position)

[1-17] 1-(1-(Meth)acryloyloxy-1-methylpropyl)adamantane (R is H or CH₃; R² is CH₃; R³ is CH₂CH₃; and Z is adamantane ring)

10 [1-18]

1-Hydroxy-3-(1-(meth)acryloyloxy-1-methylpropyl)adamantane (R is H or CH₃; R² is CH₃; R³ is CH₂CH₃; and Z is adamantane ring having hydroxyl group at the 1-position)

[1-19] 1-(1-(Meth)acryloyloxy-1,2-dimethylpropyl)adamantane

15 (R is H or CH₃; R² is CH₃; R³ is CH(CH₃)₂; and Z is adamantane ring)

[1-20]

1-Hydroxy-3-(1-(meth)acryloyloxy-1,2-dimethylpropyl)adamantane (R is H or CH₃; R² is CH₃; R³ is CH(CH₃)₂; and Z is adamantane ring having hydroxyl group at the 1-position)

[1-21]

1,3-Dihydroxy-5-(1-(meth)acryloyloxy-1-methylethyl)adamantane (R is H or CH₃; R² and R³ are CH₃; and Z is adamantane ring having hydroxyl groups at the 1- and 3-positions)

25 [1-22]

1-(1-Ethyl-1-(meth)acryloyloxypropyl)-3,5-dihydroxyadamantane (R is H or CH₃; R² and R³ are CH₂CH₃; and Z is adamantane ring having hydroxyl groups at the 3- and 5-positions)

[1-23]

5 1,3-Dihydroxy-5-(1-(meth)acryloyloxy-1-methylpropyl)adamantane (R is H or CH₃; R² is CH₃; R³ is CH₂CH₃; and Z is adamantane ring having hydroxyl groups at the 1- and 3-positions)

[1-24]

10 1,3-Dihydroxy-5-(1-(meth)acryloyloxy-1,2-dimethylpropyl)adamantane (R is H or CH₃; R² is CH₃; R³ is CH(CH₃)₂; and Z is adamantane ring having hydroxyl groups at the 1- and 3-positions)

15 Each of the compounds represented by Formula (1b) can be prepared, for example, by reacting a corresponding methanol derivative having an alicyclic group at the 1-position with (meth)acrylic acid or a reactive derivative thereof according to a conventional esterification procedure using an acid catalyst or a transesterification catalyst.

Typical examples of the compounds represented by Formula (1c) include, but are not limited to, the following compounds.

20 [1-25] 1-t-Butoxycarbonyl-3-(meth)acryloyloxyadamantane (R is H or CH₃; R⁴ is t-butoxycarbonyl group; n is 1; and Z is adamantane ring)

[1-26]

25 1,3-Bis(t-butoxycarbonyl)-5-(meth)acryloyloxyadamantane [R is H or CH₃; R⁴s are t-butoxycarbonyl groups; n is 2; and Z is

adamantane ring]

[1-27]

1-t-Butoxycarbonyl-3-hydroxy-5-(meth)acryloyloxyadamantane

(R is H or CH₃; R⁴s are OH and t-butoxycarbonyl group,

5 respectively; n is 2; and Z is adamantane ring)

[1-28]

1-(2-Tetrahydropyranyloxycarbonyl)-3-(meth)acryloyloxyadam

antane (R is H or CH₃; R⁴ is 2-tetrahydropyranyloxycarbonyl
group; n is 1; and Z is adamantane ring)

10 [1-29]

1,3-Bis(2-tetrahydropyranyloxycarbonyl)-5-(meth)acryloylox
yadamantane (R is H or CH₃; R⁴s are

2-tetrahydropyranyloxycarbonyl groups; n is 2; and Z is
adamantane ring)

15 [1-30]

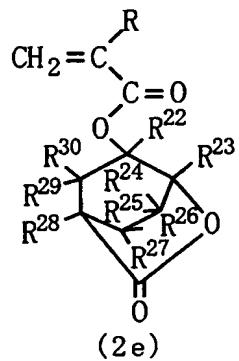
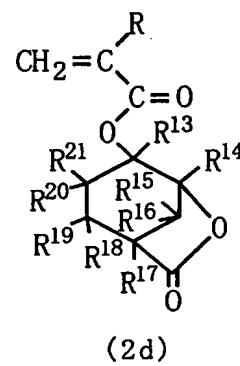
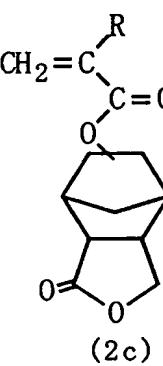
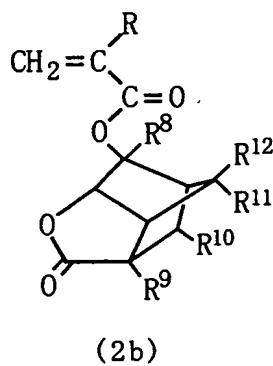
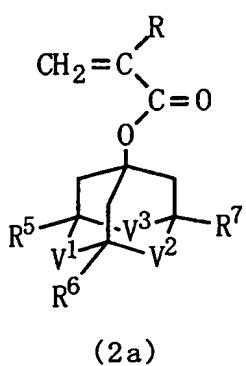
1-Hydroxy-3-(2-tetrahydropyranyloxycarbonyl)-5-(meth)acryl
oxyloxyadamantane (R is H or CH₃; R⁴s are OH and
2-tetrahydropyranyloxycarbonyl group, respectively; n is 2;
and Z is adamantane ring)

20 Each of the compounds represented by Formula (1c) can be
prepared, for example, by reacting a corresponding cyclic
alcohol with (meth)acrylic acid or a reactive derivative thereof
according to a conventional esterification procedure using an
acid catalyst or a transesterification catalyst.

25 [Constitutional Repeating Units Represented by Formulae

(IIa), (IIb), (IIc), (IId) and (IIe)]

Monomers corresponding to the constitutional repeating units represented by Formulae (IIa), (IIb), (IIc), (IId) and (IIe) are represented by following Formulae (2a), (2b), (2c),
5 (2d) and (2e), respectively. There can be stereoisomers in the compounds represented by Formulae (2a), (2b), (2c), (2d) and (2e), and each of these compounds can be used alone or in combination as a mixture.



10 Wherein R is hydrogen atom or methyl group; R⁵, R⁶ and R⁷ may be the same as or different from one another and are each hydrogen atom, an alkyl group, a hydroxyl group which may be protected

by a protective group, a hydroxyalkyl group which may be protected by a protective group, or a carboxyl group which may be protected by a protective group; V¹, V² and V³ may be the same as or different from one another and are each -CH₂-, -CO-

5 or -COO-, wherein (i) at least one of V¹, V² and V³ is -CO- or -COO-, or (ii) at least one of R⁵, R⁶ and R⁷ is a hydroxyl group which may be protected by a protective group, a hydroxyalkyl group which may be protected by a protective group, or a carboxyl group which may be protected by a protective group; R⁸, R⁹, R¹⁰,

10 R¹¹ and R¹² may be the same as or different from one another and are each hydrogen atom, an alkyl group, a hydroxyl group which may be protected by a protective group, a hydroxyalkyl group which may be protected by a protective group, or a carboxyl group which may be protected by a protective group; R¹³, R¹⁴,

15 R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰ and R²¹ may be the same as or different from one another and are each hydrogen atom, an alkyl group, a hydroxyl group which may be protected by a protective group, a hydroxyalkyl group which may be protected by a protective group, or a carboxyl group which may be protected by a protective group;

20 and R²², R²³, R²⁴, R²⁵, R²⁶, R²⁷, R²⁸, R²⁹ and R³⁰ may be the same as or different from one another and are each hydrogen atom, an alkyl group, a hydroxyl group which may be protected by a protective group, a hydroxyalkyl group which may be protected by a protective group, or a carboxyl group which may

25 be protected by a protective group.

Typical examples of the compounds represented by Formula

(2a) include, but are not limited to, the following compounds.

[2-1]

1-(Meth)acryloyloxy-4-oxatricyclo[4.3.1.1^{3,8}]undecan-5-one

5 (R is H or CH₃; R⁵, R⁶ and R⁷ are H; V² is -CO-O- (the left side
is the side of the carbon atom to which R⁶ is bonded); and V¹
and V³ are -CH₂-)

[2-2]

1-(Meth)acryloyloxy-4,7-dioxatricyclo[4.4.1.1^{3,9}]dodecane-5

10 ,8-dione (R is H or CH₃; R⁵, R⁶ and R⁷ are H; V¹ is -CO-O- (the
left side is the side of the carbon atom to which R⁵ is bonded);
V² is -CO-O- (the left side is the side of the carbon atom to
which R⁶ is bonded); and V³ is -CH₂-)

[2-3]

15 1-(Meth)acryloyloxy-4,8-dioxatricyclo[4.4.1.1^{3,9}]dodecane-5

,7-dione (R is H or CH₃; R⁵, R⁶ and R⁷ are H; V¹ is -O-CO- (the
left side is the side of the carbon atom to which R⁵ is bonded);
V² is -CO-O- (the left side is the side of the carbon atom to
which R⁶ is bonded); and V³ is -CH₂-)

20 [2-4]

1-(Meth)acryloyloxy-5,7-dioxatricyclo[4.4.1.1^{3,9}]dodecane-4

,8-dione (R is H or CH₃; R⁵, R⁶ and R⁷ are H; V¹ is -CO-O- (the
left side is the side of the carbon atom to which R⁵ is bonded);
V² is -O-CO- (the left side is the side of the carbon atom to
which R⁶ is bonded); and V³ is -CH₂-)

[2-5] 1-(Meth)acryloyloxy-3-hydroxyadamantane (R is H or CH₃; R⁵ is OH; R⁶ and R⁷ are H; and V¹, V² and V³ are -CH₂-)

[2-6] 1-(Meth)acryloyloxy-3,5-dihydroxyadamantane (R is H or CH₃; R⁵ and R⁶ are OH; R⁷ is H; and V¹, V² and V³ are -CH₂-)

5 [2-7] 1-(Meth)acryloyloxy-3,5,7-trihydroxyadamantane (R is H or CH₃, R⁵, R⁶ and R⁷ are OH; and V¹, V² and V³ are -CH₂-)

[2-8] 1-(Meth)acryloyloxy-3-hydroxy-5,7-dimethyladamantane (R is H or CH₃; R⁵ is OH; R⁶ and R⁷ are CH₃; and V¹, V² and V³ are -CH₂-)

10 [2-9] 1-(Meth)acryloyloxy-3-carboxyadamantane (R is H or CH₃; R⁵ is COOH; R⁶ and R⁷ are H; and V¹, V² and V³ are -CH₂-)

Each of the compounds represented by Formula (2a) can be prepared, for example, by reacting a corresponding cyclic alcohol derivative with (meth)acrylic acid or a reactive derivative thereof according to a conventional esterification procedure using an acid catalyst or a transesterification catalyst.

Typical examples of the compounds represented by Formula (2b) include, but are not limited to, the following compounds.

20 [2-10]

5-(Meth)acryloyloxy-3-oxatricyclo[4.2.1.0^{4,8}]nonan-2-one
(i.e., 5-(meth)acryloyloxy-2,6-norbornanecarbolactone) (R is H or CH₃; and R⁸, R⁹, R¹⁰, R¹¹ and R¹² are H)

[2-11]

25 5-(Meth)acryloyloxy-5-methyl-3-oxatricyclo[4.2.1.0^{4,8}]nonan-

-2-one (R is H or CH₃; R⁸ is CH₃; and R⁹, R¹⁰, R¹¹ and R¹² are H)

[2-12]

5-(Meth)acryloyloxy-1-methyl-3-oxatricyclo[4.2.1.0^{4,8}]nonan

5 -2-one (R is H or CH₃; R⁹ is CH₃; and R⁸, R¹⁰, R¹¹ and R¹² are H)

[2-13]

5-(Meth)acryloyloxy-9-methyl-3-oxatricyclo[4.2.1.0^{4,8}]nonan

-2-one (R is H or CH₃; R¹⁰ is CH₃; and R⁸, R⁹, R¹¹ and R¹² are

10 H)

[2-14]

5-(Meth)acryloyloxy-9-carboxy-3-oxatricyclo[4.2.1.0^{4,8}]nona

n-2-one (R is H or CH₃; R⁸, R⁹, R¹¹ and R¹² are H; and R¹⁰ is COOH)

[2-15]

15 5-(Meth)acryloyloxy-9-methoxycarbonyl-3-oxatricyclo[4.2.1.
0^{4,8}]nonan-2-one (R is H or CH₃; R⁸, R⁹, R¹¹ and R¹² are H; and
R¹⁰ is methoxycarbonyl group)

[2-16]

5-(Meth)acryloyloxy-9-ethoxycarbonyl-3-oxatricyclo[4.2.1.0

20 4,8]nonan-2-one (R is H or CH₃; R⁸, R⁹, R¹¹ and R¹² are H; and
R¹⁰ is ethoxycarbonyl group)

[2-17]

5-(Meth)acryloyloxy-9-t-butoxycarbonyl-3-oxatricyclo[4.2.1.

.0^{4,8}]nonan-2-one (R is H or CH₃; R⁸, R⁹, R¹¹ and R¹² are H; and

25 R¹⁰ is t-butoxycarbonyl group)

Each of the compounds represented by Formula (2b) can be prepared, for example, by reacting a corresponding cyclic alcohol derivative with (meth)acrylic acid or a reactive derivative thereof according to a conventional esterification procedure using an acid catalyst or a transesterification catalyst. The cyclic alcohol derivative used as a raw material can be prepared, for example, by subjecting a corresponding 5-norbornene-2-carboxylic acid derivative or an ester thereof to reaction (epoxidation and cyclization) with a peracid or a peroxide. Examples of the peracid are peracetic acid and m-chloroperbenzoic acid. Examples of the peroxide are hydrogen peroxide or a mixture of hydrogen peroxide and a metal compound such as tungsten oxide or tungstic acid.

Typical examples of the compounds represented by Formula (2c) include, but are not limited to, the following compounds.

[2-18]

8-(Meth)acryloyloxy-4-oxatricyclo[5.2.1.0^{2,6}]decan-5-one
(R is H or CH₃)

[2-19]

9-(Meth)acryloyloxy-4-oxatricyclo[5.2.1.0^{2,6}]decan-5-one
(R is H or CH₃)

Each of the compounds represented by Formula (2c) can be prepared, for example, by reacting a corresponding cyclic alcohol derivative with (meth)acrylic acid or a reactive derivative thereof according to a conventional esterification

procedure using an acid catalyst or a transesterification catalyst.

Typical examples of the compounds represented by Formula (2d) include, but are not limited to, the following compounds.

5 [2-20] 4-(Meth)acryloyloxy-6-oxabicyclo[3.2.1]octan-7-one
(R is H or CH₃; and R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰ and R²¹
are H)

[2-21]

4-(Meth)acryloyloxy-4-methyl-6-oxabicyclo[3.2.1]octan-7-one
10 e (R is H or CH₃; R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰ and R²¹ are H;
and R¹³ is CH₃)

[2-22]

4-(Meth)acryloyloxy-5-methyl-6-oxabicyclo[3.2.1]octan-7-one
e (R is H or CH₃; R¹³, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰ and R²¹ are H;
15 and R¹⁴ is CH₃)

[2-23]

4-(Meth)acryloyloxy-4,5-dimethyl-6-oxabicyclo[3.2.1]octan-
7-one (R is H or CH₃; R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰ and R²¹ are H;
and R¹³ and R¹⁴ are CH₃)

20 Typical examples of the compounds represented by Formula (2e) include, but are not limited to, the following compounds.

[2-24] 6-(Meth)acryloyloxy-2-oxabicyclo[2.2.2]octan-3-one
(R is H or CH₃; and R²², R²³, R²⁴, R²⁵, R²⁶, R²⁷, R²⁸, R²⁹ and R³⁰
are H)

25 [2-25]

6-(Meth)acryloyloxy-6-methyl-2-oxabicyclo[2.2.2]octan-3-one (R is H or CH₃; R²², R²⁴, R²⁵, R²⁶, R²⁷, R²⁸, R²⁹ and R³⁰ are H; and R²³ is CH₃)

[2-26]

5 6-(Meth)acryloyloxy-1-methyl-2-oxabicyclo[2.2.2]octan-3-one (R is H or CH₃; R²³, R²⁴, R²⁵, R²⁶, R²⁷, R²⁸, R²⁹ and R³⁰ are H; and R²² is CH₃)

[2-27]

10 6-(Meth)acryloyloxy-1,6-dimethyl-2-oxabicyclo[2.2.2]octan-3-one (R is H or CH₃; and R²⁴, R²⁵, R²⁶, R²⁷, R²⁸, R²⁹ and R³⁰ are H; and R²² and R²³ are CH₃)

Each of the compounds represented by Formulae (2d) and (2e) can be prepared, for example, by reacting a corresponding cyclic alcohol derivative with (meth)acrylic acid or a reactive derivative thereof according to a conventional esterification procedure using an acid catalyst or a transesterification catalyst.

The resulting polymer formed as a result of polymerization can be isolated by precipitation or reprecipitation. The target polymer, for example, can be obtained by adding a polymerization solution (polymer dope) to a solvent (precipitation solvent) to thereby precipitate a polymer, or by dissolving the precipitated polymer in an appropriate solvent to yield a solution, and adding the solution to a solvent (reprecipitation solvent) to thereby reprecipitate the polymer.

The precipitation solvent or reprecipitation solvent may be any of organic solvents and water, or mixtures of these solvents. Examples of the organic solvents for use as the precipitation solvent or reprecipitation solvent are hydrocarbons including
5 aliphatic hydrocarbons such as pentane, hexane, heptane and octane, alicyclic hydrocarbons such as cyclohexane and methylcyclohexane, and aromatic hydrocarbons such as benzene, toluene and xylenes; halogenated hydrocarbons including halogenated aliphatic hydrocarbons such as methylene chloride,
10 chloroform and carbon tetrachloride, and halogenated aromatic hydrocarbons such as chlorobenzene and dichlorobenzene; nitro compounds such as nitromethane and nitroethane; nitriles such as acetonitrile and benzonitrile; ethers including open-chain ethers such as diethyl ether, diisopropyl ether and
15 dimethoxyethane, and cyclic ethers such as tetrahydrofuran and dioxane; ketones such as acetone, methyl ethyl ketone and diisobutyl ketone; esters such as ethyl acetate and butyl acetate; carbonates such as dimethyl carbonate, diethyl carbonate, ethylene carbonate and propylene carbonate;
20 alcohols such as methanol, ethanol, propanol, isopropanol and butanol; carboxylic acids such as acetic acid; and mixtures containing these solvents.

Among them, solvents each containing at least a hydrocarbon, preferably an aliphatic hydrocarbon such as hexane or heptane,
25 are preferred as the organic solvents for use as the

precipitation solvent or reprecipitation solvent. The ratio of the hydrocarbon (e.g., an aliphatic hydrocarbon such as hexane or heptane) to the other solvent (e.g., an ester such as ethyl acetate) in the solvent containing at least a hydrocarbon is, 5 for example, from about 10/90 to about 99/1, preferably from about 30/70 to about 98/2, and more preferably from about 50/50 to about 97/3 in terms of volume ratio at 25°C.

If desired, the polymer obtained by precipitation or reprecipitation is subjected to repulping and/or rinsing. It 10 may be subjected to rinsing after repulping. By repulping and/or rinsing the polymer prepared by polymerization, residual monomers and low-molecular oligomers attached to the polymer can be removed efficiently. In addition, the resulting polymer particles have hardened surfaces and are prevented from fusing 15 with each other during subsequent processes such as drying process. This is probably because a high-boiling solvent having affinity for the polymer has been removed. Thus, the polymer becomes significantly highly soluble in solvents for resist, which enables a photoresist resin compositions to be 20 prepared easily and efficiently.

The solvent for repulping (repulping solvent) and the solvent for rinsing (rinsing solvent) are preferably poor solvents for the polymer which may be used in precipitation or reprecipitation. Among them, hydrocarbon solvents are 25 typically preferred. Examples of such hydrocarbon solvents

are alicyclic hydrocarbons such as pentane, hexane, heptane and octane; alicyclic hydrocarbons such as cyclohexane and methylcyclohexane; and aromatic hydrocarbons such as benzene, toluene and xylenes. Each of these can be used in combination 5 as a mixture. Among them, one or more alicyclic hydrocarbons are preferred, of which heptane or hexane, or mixtures containing hexane or heptane are typically preferred.

The amount of the repulping solvent is, for example, from about 1 to about 200 times by weight, and preferably from about 10 5 to about 100 times by weight, the weight of the polymer. The amount of the rinsing solvent is, for example, from about 1 to about 100 times by weight, and preferably from about 2 to about 20 times by weight, the weight of the polymer. The temperature for the repulping and/or rinsing is generally from 15 about 0°C to about 100°C, and preferably from about 10°C to about 60°C, while varying depending typically on the type of a solvent to be used. The repulping and/or rinsing is carried out in an appropriate vessel. The repulping and rinsing procedures may be repeated plural times, respectively. The liquids after 20 treatment (repulping liquid or rinsing liquid) are removed, for example, by decantation or filtration.

The resulting wet polymer after precipitation or reprecipitation, or further after repulping and/or rinsing according to necessity is then subjected to drying. The drying 25 temperature is, for example, from about 20°C to about 120°C,

and preferably from about 40°C to about 100°C. The drying is preferably carried out under reduced pressure at, for example, 200 mmHg (26.6 kPa) or less, and more preferably at 100 mmHg (13.3 kPa) or less.

5 The above-mentioned process yields a photoresist resin which has a weight-average molecular weight of 3000 to 15000 and has a content of polymer fractions each having a molecular weight exceeding 40000 of 4 percent by weight or less of the total resin. The weight-average molecular weight can be
10 controlled by appropriately adjusting, for example, the monomer composition, amount of the polymerization initiator, polymerization temperature and/or polymerization time.

The turbidity of the resulting photoresist resin is generally from about 0 to about 10, preferably from about 0
15 to about 3, more preferably from about 0 to about 1, and typically preferably from about 0 to about 0.1. The turbidity herein is determined by mixing 1 gram of a sample photoresist resin with 19 grams of polypropylene glycol monomethyl ether acetate (PGMEA), shaking the resulting mixture at room temperature for
20 60 minutes to yield a resin mixture having a resin concentration of 5 percent by weight, and measuring the turbidity of the resin mixture according to Japanese Industrial Standards (JIS) K 0101 (integrating-sphere turbidity).

The photoresist resin composition of the present invention
25 comprises a light-activatable acid generator in addition to

the photoresist resin of the present invention. As the light-activatable acid generator, any of conventional or known compounds that efficiently generate an acid upon irradiation of light can be used. Examples of such compounds are diazonium salts; iodonium salts such as diphenyliodohexafluorophosphate; sulfonium salts such as triphenylsulfonium hexafluoroantimonate, triphenylsulfonium hexafluorophosphate and triphenylsulfonium methanesulfonate; sulfonic acid esters such as
10 1-phenyl-1-(4-methylphenyl)sulfonyloxy-1-benzoylmethane, 1,2,3-trisulfonyloxymethylbenzene, 1,3-dinitro-2-(4-phenylsulfonyloxymethyl)benzene and 1-phenyl-1-(4-methylphenylsulfonyloxymethyl)-1-hydroxy-1-benzoylmethane; oxathiazole derivatives; s-triazine
15 derivatives; disulfone derivatives such as diphenyl disulfone; imide compounds; oxime sulfonates; diazonaphthoquinone; and benzoin tosylate. Each of these light-activatable acid generators can be used alone or in combination.

The amount of the light-activatable acid generator can
20 be appropriately set according to, for example, the intensity of an acid formed upon irradiation of light and/or the proportions of respective constitutional repeating units in the polymer (photoresist resin) and is, for example, from about 0.1 to about 30 parts by weight, preferably from about 1 to
25 about 25 parts by weight, and more preferably from about 2 to

about 20 parts by weight, to 100 parts by weight of the polymer.

The photoresist resin composition may further comprise any of other components. Examples of such components are alkali-soluble components including alkali-soluble resins such as novolak resins, phenol resins, imide resins and carboxyl-containing resins; coloring agents such as dyes; and organic solvents such as hydrocarbons, halogenated hydrocarbons, alcohols, esters, amides, ketones, ethers, Cellosolves, Carbitols, glycol ether esters, and mixtures of these solvents.

The photoresist resin composition of the present invention can be prepared by dissolving the photoresist resin of the present invention in a solvent (solvent for photoresist). More specifically, the photoresist resin composition can be prepared by adding the photoresist resin of the present invention as intact, or after an appropriate purification procedure according to necessity, to an organic solvent, and mixing and stirring them together with a light-activatable acid generator and other components, if added.

A fine pattern can be formed with high accuracy by applying the resulting photoresist resin composition to a base or substrate to form a coating, drying the coating, applying radiation rays to the coating (resist film), or further baking after light irradiation, to form a latent image pattern, and developing the latent image pattern.

Examples of the base or substrate are silicon wafers, metals, plastics, glass and ceramics. The photoresist resin composition can be applied using a conventional coating device such as a spin coater, a dip coater or a roller coater. The 5 thickness of the coating is, for example, from about 0.1 to about 20 μm , and preferably from about 0.3 to about 2 μm .

Radiation rays of various wavelengths, such as ultraviolet rays or X-rays, can be used for light irradiation (exposure). For semiconductor resists, g-line, i-line or excimer laser such 10 as XeCl, KrF, KrCl, ArF or ArCl is generally used. The exposure energy is, for example, from about 1 to about 1000 mJ/cm^2 , and preferably from about 10 to about 500 mJ/cm^2 .

The light-activatable acid generator generates an acid upon irradiation with light. By the action of the acid, a 15 protective group (leaving group), for example, of a carboxyl group in the constitutional repeating unit capable of partially leaving by the action of an acid to thereby become soluble in an alkali in the photoresist resin rapidly leaves to thereby yield, for example, a carboxyl group that contributes to render 20 the polymer soluble. Thus, a predetermined pattern can be formed accurately as a result of development with water or an alkali developing agent.

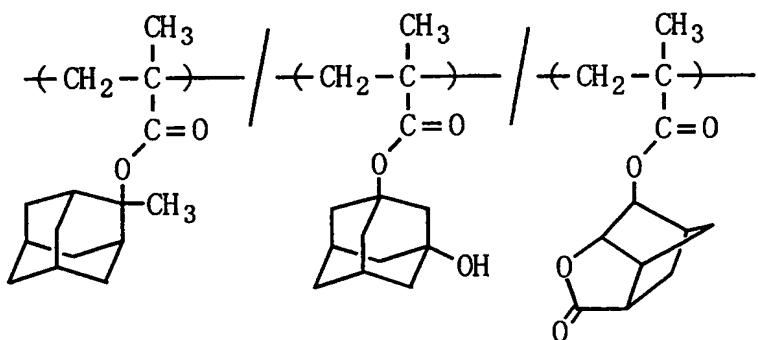
EXAMPLES

25 The present invention will be illustrated in further detail

with reference to several examples below, which are not intended to limit the scope of the invention. The indication "acrylate" after a compound number (a monomer number) represents a compound having acryloyloxy group between two compounds corresponding 5 to the compound number described in the description, and the indication "methacrylate" represents a compound having methacryloyl group between the two compounds. The weight-average molecular weight (M_w), the molecular weight distribution (M_w/M_n) and the content of polymer fractions each 10 having a molecular weight exceeding 40000 were determined in terms of standard polystyrene by GPC using a refractometer (RI) as a detector and tetrahydrofuran (THF) as an eluent. The GPC determination was carried out using three columns "Shodex KF-806L" (trade name) available from Showa Denko K.K. connected 15 in series under conditions at a sample concentration of 0.5%, amount of injected sample of 35 μm , column temperature of 40°C, RI temperature of 40°C, flow rate of eluent of 0.8 ml/min., and analysis time of 60 minutes. An apparatus "GPCLC-10A" available from Shimadzu Corporation was used as a GPC analyzer.

20 EXAMPLE 1

Preparation of Photoresist Resin Having the Following
Structure



In a reactor equipped with a stirrer, a thermometer, a reflux condenser, two dropping vessels and a nitrogen inlet tube was charged 2500 g of propylene glycol monomethyl ether acetate (PGMEA) and was heated to 77°C. A monomer solution and a polymerization initiator solution were then added dropwise to the reactor from different dropping vessels using metering pumps, respectively, over six hours. The monomer solution contained 500 g of 1-hydroxy-3-methacryloyloxyadamantane (HMA)

5 [Compound Number [2-5] (methacrylate)], 500 g of 5-methacryloyloxy-2,6-norbornanecarbolactone (MNBL) [Compound Number [2-10] (methacrylate)] and 500 g of 2-methacryloyloxy-2-methyladamantane (2MMA) [Compound Number [1-1] (methacrylate)] dissolved in 4000 g of propylene glycol monomethyl ether acetate (PGMEA). The polymerization

10 initiator solution contained 93 g of dimethyl-2,2'-azobis(2-methylpropionate) (initiator; V-601, available from Wako Pure Chemical Industries, Ltd.) dissolved in 900 g of propylene glycol monomethyl ether acetate (PGMEA).

15 As the temperature gradually fell after the beginning of dropping,

20

the preset temperature of a control system was gradually reduced to 75°C and was held to 75°C thereafter. The liquid temperature fell from 77°C to 75°C in ten minutes after the beginning of dropping. The polymerization temperature (temperature of the reaction mixture) could be held within 75°C±1°C from ten minutes to six hours after the beginning of the dropping. After the completion of dropping, the reaction mixture was aged at the same temperature for two hours. The polymerization reaction mixture was added dropwise to a mixture containing 65000 g of heptane and 21500 g of ethyl acetate at ordinary temperature, followed by stirring for thirty minutes and standing still for ninety minutes. The supernatant was taken out, and the residue was mixed with 64000 g of heptane, followed by repulping at ordinary temperature. This procedure was carried out a total of two times. The residue from which the supernatant had been taken out was transferred to a centrifugal separator, followed by drainage by the action of centrifugal force, to yield a wet polymer. The wet polymer was mixed with 6500 g of heptane, was rinsed in a centrifugal separator, and the rinsing liquid was removed. The resulting wet polymer was taken out, was subjected to vacuum drying at 50°C, 20 mmHg (2.66 kPa) and thereby yielded 100 g of the target resin. The recovered resin was subjected to GPC analysis and was found to have a weight-average molecular weight (M_w) of 9100, a molecular weight distribution (M_w/M_n) of 1.8, and a content of polymer fractions each having

a molecular weight exceeding 40000 of 1.2 percent by weight.

EXAMPLE 2

Preparation of Photoresist Resin Having the same Structure
as Example 1

5 In a separable flask equipped with a stirrer, a thermometer,
a reflux condenser, two dropping funnels and a nitrogen inlet
tube was charged 25 g of propylene glycol monomethyl ether
acetate (PGMEA) and was heated to 77°C. A monomer solution and
a polymerization initiator solution were then added dropwise
10 to the separable flask from different dropping funnels,
respectively, over six hours. The monomer solution contained
5 g of 1-hydroxy-3-methacryloyloxyadamantane (HMA) [Compound
Number [2-5] (methacrylate)], 5 g of
5-methacryloyloxy-2,6-norbornanecarbolactone (MNBL)
15 [Compound Number [2-10] (methacrylate)] and 5 g of
2-methacryloyloxy-2-methyladamantane (2MMA) [Compound Number
[1-1] (methacrylate)] dissolved in 40 g of propylene glycol
monomethyl ether acetate (PGMEA). The polymerization
initiator solution contained 0.93 g of
20 dimethyl-2,2'-azobis(2-methylpropionate) (initiator; V-601,
available from Wako Pure Chemical Industries, Ltd.) dissolved
in 9 g of propylene glycol monomethyl ether acetate (PGMEA).
As the temperature gradually fell after the beginning of dropping,
the preset temperature of a control system was gradually reduced
25 to 75°C and was held to 75°C thereafter. The liquid temperature

fell from 77°C to 75°C in ten minutes after the beginning of dropping. The polymerization temperature (temperature of the reaction mixture) could be held within 75°C±1°C from ten minutes to six hours after the beginning of the dropping. After the completion 5 of dropping, the reaction mixture was aged at the same temperature for two hours. The polymerization reaction mixture was added dropwise to a mixture containing 650 g of heptane and 215 g of ethyl acetate at ordinary temperature, followed by stirring for thirty minutes and standing still for ninety 10 minutes. The supernatant was taken out, and the residue was mixed with 640 g of heptane, followed by repulping at ordinary temperature. This procedure was carried out a total of two times. The residue from which the supernatant had been taken out was transferred to a centrifugal separator, followed by 15 drainage by the action of centrifugal force, to yield a wet polymer. The wet polymer was mixed with 65 g of heptane, was rinsed in a centrifugal separator, and the rinsing liquid was removed. The resulting wet polymer was taken out, was subjected to vacuum drying at 50°C, 20 mmHg (2.66 kPa) and thereby yielded 20 11 g of the target resin. The recovered resin was subjected to GPC analysis and was found to have a weight-average molecular weight (M_w) of 9100, a molecular weight distribution (M_w/M_n) of 1.8, and a content of polymer fractions each having a molecular weight exceeding 40000 of 1.2 percent by weight.

25 COMPARATIVE EXAMPLE 1

Preparation of Photoresist Resin Having the same Structure
as Example 1

In a separable flask equipped with a stirrer, a thermometer, a reflux condenser, a dropping funnel and a nitrogen inlet tube 5 was charged 33 g of propylene glycol monomethyl ether acetate (PGMEA) and was heated to 75°C. A solution mixture was then added dropwise to the separable flask from the dropping funnel over six hours. The solution mixture contained 5 g of 1-hydroxy-3-methacryloyloxyadamantane (HMA) [Compound Number 10 [2-5] (methacrylate)], 5 g of 5-methacryloyloxy-2,6-norbornanecarbolactone (MNBL) [Compound Number [2-10] (methacrylate)], 5 g of 2-methacryloyloxy-2-methyladamantane (2MMA) [Compound Number [1-1] (methacrylate)], 0.93 g of 15 dimethyl-2,2'-azobis(2-methylpropionate) (initiator; V-601, available from Wako Pure Chemical Industries, Ltd.) and 41 g of propylene glycol monomethyl ether acetate (PGMEA). The temperature was controlled while setting the preset temperature of the control system at 75°C. However, the liquid temperature 20 significantly fell below 70°C at the beginning of dropping. Thus, the deviation of the polymerization temperature (temperature of reaction mixture) was out of a range of $\pm 5^\circ\text{C}$ of the preset temperature 75°C during the first thirty minutes (8.3% of the total dropping time) of the total dropping time (six hours) 25 of the mixture solution containing the monomers and the

polymerization initiator. The polymerization temperature (temperature of the reaction mixture) could be held within $75^{\circ}\text{C} \pm 1^{\circ}\text{C}$ from thirty minutes after the beginning of the dropping. After the completion of dropping, the reaction mixture was aged 5 at the same temperature for two hours. The polymerization reaction mixture was added dropwise to a mixture containing 650 g of heptane and 215 g of ethyl acetate at ordinary temperature, followed by stirring for thirty minutes and standing still for ninety minutes. The supernatant was taken out, and the residue 10 was mixed with 640 g of heptane, followed by repulping at ordinary temperature. This procedure was carried out a total of two times. The residue from which the supernatant had been taken out was transferred to a centrifugal separator, followed by drainage by the action of centrifugal force, to yield a wet 15 polymer. The wet polymer was mixed with 65 g of heptane, was rinsed in a centrifugal separator, and the rinsing liquid was removed. The resulting wet polymer was taken out, was subjected to vacuum drying at 50°C , 20 mmHg (2.66 kPa) and thereby yielded 10 g of the target resin. The recovered resin was subjected 20 to GPC analysis and was found to have a weight-average molecular weight (M_w) of 9700, a molecular weight distribution (M_w/M_n) of 3.1, and a content of polymer fractions each having a molecular weight exceeding 40000 of 4.7 percent by weight.

Evaluation Test

25 Each 1 gram of the resins obtained according to the examples

and comparative example was mixed with 19 grams of propylene glycol monomethyl ether acetate (PGMEA), followed by shaking at room temperature for sixty minutes, to yield resin mixtures each having a resin concentration of 5 percent by weight. The 5 turbidities of the resin mixtures were determined according to JIS K 0101 (integrating-sphere turbidity) using a haze turbidimeter [trade name of "NDH 300A", available from Nippon Denshoku Industries Co., Ltd.]. The resins according to Examples 1 and 2 each had a turbidity of 0.0, and the resin 10 according to Comparative Example 1 had a turbidity of 13.3, showing that there was a significant difference between the two.